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Evaluation of Solids Dewatering for a Pilot-Scale Thiosorbic Lime SO2 Scrubber

Acurex Corp., Research Triangle Park, NC

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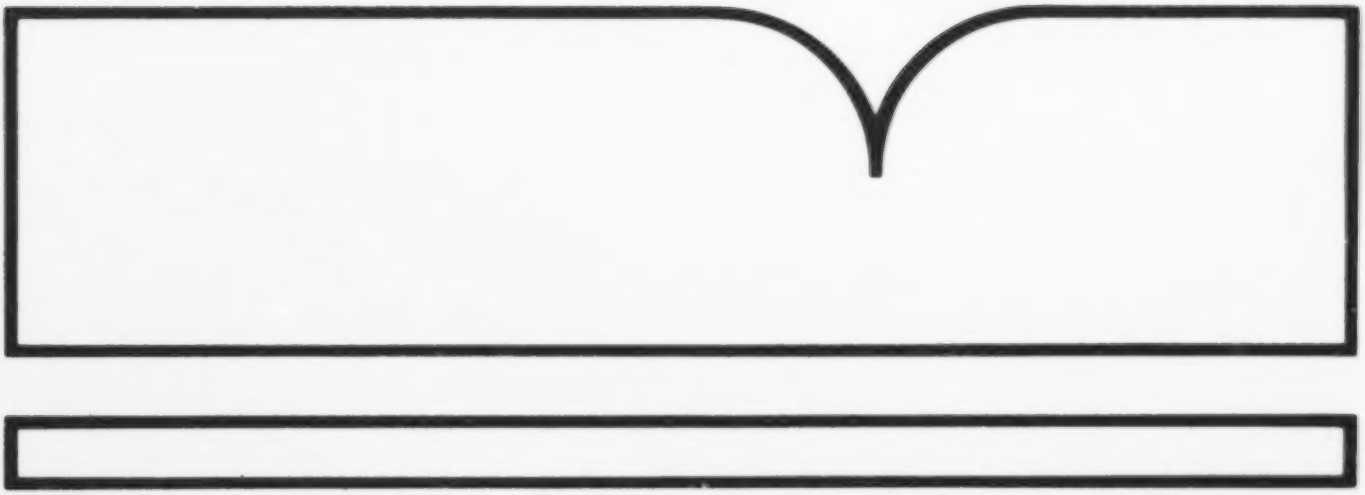

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EVALUATION OF SOLIDS DEWATERING FOR A PILOT-SCALE THIOSORBIC LIME SO_2 SCRUBBER

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16. ABSTRACT The paper gives results of an evaluation of solids dewatering for a pilot-scale thiosorbic lime SO2 scrubber. Pilot plant data showed that the dissolved magnesium in thiosorbic lime caused deterioration of solids dewatering properties. The slurry settling rate increased when the slurry shear stresses caused by the hold tank stirrer and recirculation pump were reduced. The application of flocculant also increased the slurry solids settling rate. Compared with rotary drum vacuum filtering, better liquid/solids separation occurred with a centrifuge. Other related performance results are also discussed.

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ABSTRACT

Pilot plant data showed that the dissolved magnesium in thiosorbic lime caused deterioration of solids dewatering properties. The slurry settling rate increased when the slurry shear stresses caused by the hold tank stirrer and recirculation pump were reduced. The application of flocculant also increased the slurry solids settling rate. Compared with rotary drum vacuum filtering, better liquid/solids separation occurred with a centrifuge. Other related performance results are also discussed.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Thiosorbic lime inherently has a moderate magnesium oxide content (5 to 6 wt. %). When thiosorbic lime is the reagent in a wet flue gas desulfurization (FGD) scrubber, magnesium tends to accumulate and to become the major liquor cation. One reason for this tendency is that magnesium forms more soluble salts than calcium with the major scrubber anions, sulfite and sulfate.[1] The magnesium sulfite reacts with SO_2 and greatly enhances SO_2 removal efficiency; therefore, the thiosorbic lime process is a commonly used FGD process when high sulfur coal is burned.[2] However, the scrubber product of this process is usually more difficult to dewater than the calcium sulfite hemihydrate formed in conventional (low magnesium) lime/limestone FGD processes. The solids dewatering properties directly affect the size and cost required for thickeners and filters. A poor quality solids product also increases water loss and waste load.

One approach to improve solids dewatering is to provide process conditions favorable for crystallization of calcium sulfite hemihydrate so that larger and denser crystals are produced. Crystallization theories indicate that the crystal size and shape can be affected by both chemical and mechanical operating conditions.[3] The chemical conditions include supersaturation level, the concentration of impurities, and crystal growth modifiers. The mechanical factors include the extent of collision and attrition between crystals and agitator blades, pump impeller, or hold tank wall.

Another approach is to provide favorable dewatering conditions by using additives and appropriate dewatering equipment. Flocculant can be added to thickeners to form aggregates which settle faster than the individual crystals. For solids dewatering, most utilities have traditionally used vacuum filters. However, centrifuges may offer more flexibility in handling various inlet slurry conditions and produce stable and good quality cake.[4,5]

Limited data[6] are available to address the effects of the noted approaches which may significantly affect the design and operation of the thiosorbic lime process. In order to study these effects and to expand the FGD data base, testing cosponsored by a utility company and the U. S. Environmental Protection Agency's Air and Energy Engineering Research Laboratory (EPA-AEERL) was conducted in the AEERL pilot plant at Research Triangle Park, NC. The objectives of the testing were to investigate the effects of chemical and mechanical factors on calcium sulfite hemihydrate dewatering properties, to evaluate the effectiveness of flocculant addition, and to assess the feasibility of a centrifuge for solids dewatering in the thiosorbic lime process.

TEST PROGRAM

Equipment

The pilot plant scrubber used in this work was a single stage tray column with a 7.5 m^3/min. flue gas capacity (0.1 MW). The tray was made of 0.64-cm (1/4-in.)-thick Teflon plate with 14 symmetrical 3.81-cm (1.5-in.)-diameter holes. No fly ash was present in the flue gas, which was drawn from a gas-fired boiler and injected with pure SO_2. The pilot plant was equipped with a clarifier, a filtrate tank, and a rotary drum vacuum filter as shown in Figure 1. The filtrate recycle rate was adjusted to simulate either the open- or closed-loop operating mode. The hold tank pH was controlled by adjusting the thiosorbic lime slurry feed rate.

Test Plan

The operating conditions for the tests conducted are listed in Table 1. Each test consisted of approximately 100 hours of continuous operation. Throughout each test, the flue gas SO_2 concentrations were monitored continuously by an ultraviolet spectrophotometric analyzer (DuPont 400 SO_2 analyzer).

The scrubbing liquor magnesium concentration was monitored by ethylenediamine tetraacetate (EDTA) titration of liquid samples every other hour and confirmed by periodic atomic absorption spectrophotometric analyses. When needed, magnesium hydroxide was added to the hold tank, and magnesium chloride was used to adjust the chloride and magnesium concentrations. The solids dewatering properties were characterized by hold tank slurry settling rate and filter cake insoluble solids concentration. The slurry settling rate was measured in a 1,000-ml graduated cylinder by determining the average settling rate of the meniscus for a distance of 8.5 cm from the top of the cylinder. The filter cake insoluble solids concentration was determined by weighing a filter cake sample before and after drying. The sample was dried in a microwave oven for 15 minutes after being washed by deionized water. The insoluble solids concentration was defined as the weight ratio of the dry cake to wet cake.

RESULTS AND DISCUSSION

Chemical Effects

Four runs (Table 2) were made to evaluate the effects of magnesium concentration on solids dewatering properties. Run 1 was a baseline test using calcitic lime (magnesium oxide content less than 0.5%) as the alkaline reagent. For this run, the total magnesium concentration was about 290 ppm. The SO_2 removal efficiency was 73%. The hold tank slurry settling rate was 0.29 cm/min., and the filter cake solids concentration was 51 wt. %.

Thiosorbic lime was used as the alkaline reagent for Run 2. The hold tank slurry was spiked with magnesium chloride to increase the chloride concentration to about 2,000 ppm. The total magnesium concentration was controlled at about 3,200 ppm when the system stabilized. The SO_2 removal increased at the higher magnesium concentration (90% for Run 2 vs. 73% for Run 1). However, the high magnesium concentration also caused the deterioration of solids dewatering properties. Compared with Run 1, the slurry settling rate decreased from 0.29 to 0.14 cm/min., and the filter cake insoluble solids concentration also decreased from 51 to 46%. It was postulated that, probably due to the similarity between calcium and magnesium ions, the magnesium ion can be adsorbed on the surface of $CaSO_3$ crystals to form a surface Ca-Mg-sulfite.[7] The adsorbed magnesium can act as an impurity which causes crystal defects and inhibits crystal growth. It was also postulated[6] that the solids dewatering changes can be correlated with sulfite ion concentration which increases with the accumulation of magnesium. As a result, the dewatering properties of the solids product deteriorate with the increase of magnesium concentration as reflected by the decrease of slurry settling rate and filter cake insoluble solids content.

During Run 3, the hold tank was spiked with magnesium chloride to further increase the total chloride concentration to 15,000 ppm. Correspondingly, the total magnesium concentration also increased to 7,600 ppm. However, the performance results showed that both SO_2 removal efficiency and solids dewatering properties remained at about the same level as Run 2. These results suggest that only a portion of the magnesium present in the slurry affects the system performance. Burbank and Wang[8] proposed the following equation to calculate the effective magnesium concentration:

$$[Mg]_E = [Mg]_{Total} - 0.34[Cl]_{Total} \quad (1)$$

where $[Mg]_E$ denotes the effective magnesium present which impacts scrubber performance.

The effective magnesium concentrations based on Equation (1) for Runs 1, 2, and 3 are 110, 2,524, and 2,530 ppm, respectively. The pilot plant results indicated that the portion of magnesium associated with chloride can be considered as inert. Only the portion of magnesium in excess of that combined with chloride is effective in altering the system performance. Similar SO_2 removal enhancement and solids dewatering property changes can be expected at about the same effective magnesium concentrations, although the total magnesium concentrations are significantly different.

Run 4 was an unsteady-state test. Magnesium hydroxide was added to the hold tank slurry to raise the total magnesium concentration from 3,200 to 5,200 ppm in about 48 hours while the chloride concentration was maintained at 2,000 ppm. Although the SO_2 removal efficiency increased from 90 to 96% on increasing the effective magnesium concentration from 2,524 to 4,524 ppm, extremely poor solids dewatering properties were obtained. The slurry settling rate decreased to the range of 0.04 to 0.08 cm/min., and the filter cake insoluble solids concentration dropped to as low as 32 wt. %. Scanning electron micrographs (SEM) of the solids produced in Runs 2 and 4 showed distinctively different crystal morphology. Figure 2(a) indicates that the solids from Run 2 were composed of thin platelets. However, the solids from Run 4 are ill-defined, needle-like crystals with significant crystal defects as seen in Figure 2(b). It is believed that the deterioration of crystal structure resulted from the increase in the local effective magnesium concentration because of magnesium hydroxide addition/dissolution. At the end of Run 4 when the total magnesium had reached 5,200 ppm, the magnesium hydroxide addition was reduced, and the pilot plant was operated at 5,200 ppm total magnesium concentration for approximately 16 hours. For this change in

test conditions, the slurry settling rate increased slightly to about 0.1 cm/min., while the filter cake insoluble solids concentration also increased to about 40%. The improved solids properties with the decreased magnesium hydroxide addition seemed to imply that the increase of the magnesium dissolution rate per unit volume in the hold tank can degrade solids dewatering as well as increase the bulk magnesium concentration.

Mechanical Effects

Four runs were made to evaluate the effects of recirculation pump and hold tank agitator blade tip speed on solids dewatering properties. Literature data[9,10] showed that a dominant mechanism causing secondary nucleation is the high speed collision of crystals with the crystallizer (hold tank) stirrer impeller or circulating pump impeller. Attrition and breakage of crystals because of too vigorous agitation combined with long residence time has also been observed to degrade the dewatering properties of FGD solids.[11] These data suggested that the solids morphology and dewatering properties could be improved by reducing the shear stress induced by the scrubber recirculation pump and hold tank agitator.

Run 5 (Table 3) used a centrifugal pump (Galigher horizontal pump) with a 2.2 m/s (7.2 ft/sec) tip speed. A marine-type propeller with three blades was used as the hold tank agitator, and the tip speed was controlled at 16 m/s (52.5 ft/sec). In Runs 6, 7, and 8, the centrifugal pump was replaced by an air diaphragm pump (Wilden pump M4) with the hold tank agitator blade tip speed reduced to 5.6 m/s (18.3 ft/sec) for Run 6. The slurry settling rate increased to 0.15 cm/min. compared with 0.1 cm/min. in Run 5. A further increase in settling rate to 0.2 cm/min. was obtained by reducing the agitator tip speed to 3.0 m/s (10 ft/sec) in Run 7. A very low, 1.8 m/s (6 ft/sec), agitator blade tip speed was used in Run 8. However, no increase in settling rate was obtained by reducing the blade tip speed from 3.0 m/s (Run 7) to

1.8 m/s (Run 8). Table 3 also shows that the filter cake insoluble solids concentration changed slightly from Run 5 through 8. This was probably due to the short test period (less than 30 hours for each run) in which which the "old" and "new" solids tended to be mixed in the hold tank and the thickener.

Dewatering Effects

A flocculant provided by a utility company was tested in the 1,000-ml graduated cylinders. Slurry samples were taken from the hold tank and split into two portions. One 1,000-ml sample was spiked with 0.5 mg flocculant. The settling rate measurements of the slurry samples with and without flocculant were conducted simultaneously. A set of typical settling curves obtained are shown in Figure 3. The slurry with flocculant usually settled faster and reached complete sedimentation earlier than the non-flocculated slurry. However, the resulting sediment from the flocculated slurry was usually less dense and often more mobile than the non-flocculated slurry. Thus, the data indicated that the use of flocculant would promote solid/liquid separation in the thickener to generate a clearer supernate. However, the density of the thickener bottom sludge and the filter cake quality probably would not improve.

A rotary drum vacuum filter and a centrifuge were compared as solids dewatering devices. The filter was an Ametek Filtration Engineer's continuous rotary drum vacuum filter with a 3.5 rpm drum speed, while the centrifuge was a Sharples Model 660 solid-bowl type. The centrifuge and rotary drum filter were connected in parallel to permit simultaneous operation. The pilot plant test results, shown in Figure 4, indicate that the cake solids content with the centrifuge was superior to that with the vacuum filter. The centrifuge cake insoluble solids were also consistently higher than the filter cake solids. The poorest centrifuge cake contained about 48% insoluble solids, about the same as the best vacuum filter cake. Also, the centrifuge solids

product seemed to be less sensitive than that of the vacuum filter toward the quality (settling rate) of the slurry. The centrate was also very clear and usually contained less than 0.3 wt. % insoluble solids. Following the manufacturer's recommendations, the centrifuge bowl speed was set at 5,380 rpm and the speed difference between the centrifuge bowl and the internal screw conveyer was set at 18 rpm. The noise generated by the centrifuge (95 dB) posed a safety concern, which resulted in the cancelling of several tests. However, the noise problem might be peculiar to the scale of the AEERL pilot plant and the specific centrifuge model tested.

CONCLUSIONS

Conclusions drawn from the pilot plant testing of the thiosorbic lime process included:

1. The magnesium ion derived from thiosorbic lime caused the deterioration of the FGD solids product properties. When chloride ion is present in the scrubbing liquor, the magnesium associated with chloride can be considered inert. Only the portion of magnesium in excess of that associated with chloride affects the SO_2 removal efficiency and solids dewatering.
2. The data suggested that the quality of the solids product deteriorated with increased magnesium dissolution rate and local effective magnesium concentration. The pilot plant data imply that, in a utility thiosorbic lime scrubber, the solids dewatering properties may degrade when the boiler load and coal sulfur content increase.
3. The slurry settling rate can be increased by reducing the blade tip speed of the hold tank agitator and changing from a centrifugal to an air diaphragm recirculation pump.

4. Flocculant addition is effective in increasing the slurry settling rate and promoting clear supernate, but it may not improve filter cake quality.
5. A centrifuge is superior to a vacuum filter in terms of cake quality (insoluble solids content) and solids dewatering stability.

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TABLE 1. OPERATING CONDITIONS FOR EVALUATION OF SOLIDS DEWATERING PROPERTIES FOR THIOSORBIC LIME PROCESS AT THE EPA-AEERL PILOT PLANT

L/G, l/m^3 (gal/1000 ft^3)	=	8.4 (63)
Flue gas SO_2 at inlet, ppm	=	2000
Flue gas O_2 at inlet, vol.%	=	5 - 6
Hold tank solids, wt. %	=	6
Hold tank pH	=	6.5
Hold tank residence time, min.	=	6

TABLE 2. EFFECTS OF MAGNESIUM CONCENTRATIONS ON THIOSORBIC LIME PILOT PLANT PERFORMANCE

Run No.	1	2	3	4
Lime type	Calcitic	Thiosorbic	Thiosorbic	Thiosorbic
$Mg(OH)_2$ addition	No	No	No	Yes
Total magnesium, ppm	290	3,200	7,600	3,200-5,200
Effective magnesium, ppm	253	2,524	2,530	2,524-4,524
Total chloride, ppm	110	2,000	15,000	2,000
SO_2 removal, %	73	90	90	90-96
Settling rate, cm/min.	0.29	0.14	0.15	0.04-0.08
Filter cake solids, wt. %	51	46	46	32-38

TABLE 3. EFFECTS OF MECHANICAL CONDITIONS ON SOLIDS DEWATERING PROPERTIES OF THIOSORBIC LIME PILOT PLANT

Run No.	5	6	7	8
Lime type	Thiosorbic	Thiosorbic	Thiosorbic	Thiosorbic
$Mg(OH)_2$ addition	No	No	No	No
Effective magnesium, ppm	2500	2500	2500	2500
Pump type	Centrifugal	Diaphragm	Diaphragm	Diaphragm
Agitator blade tip speed, m/s	16	5.6	3.0	1.8
Settling rate, cm/min.	0.1	0.15	0.2	0.2
Filter cake solids, wt. %	48	48	47	48

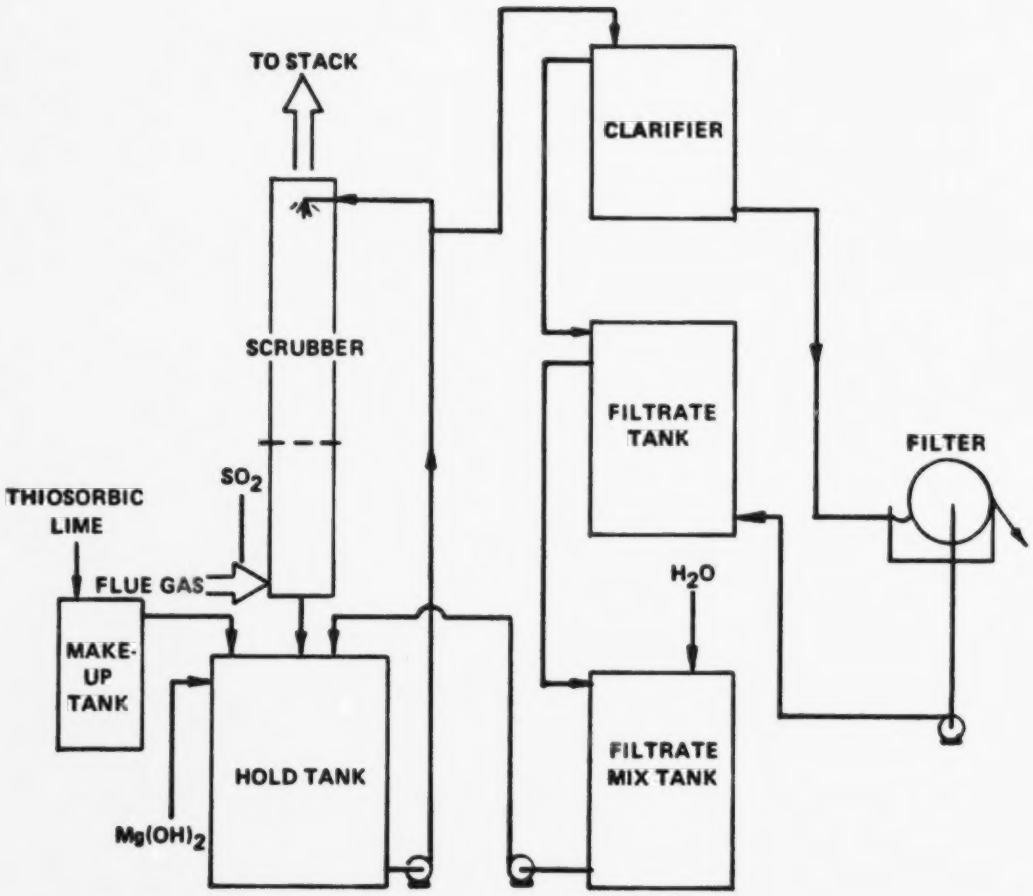
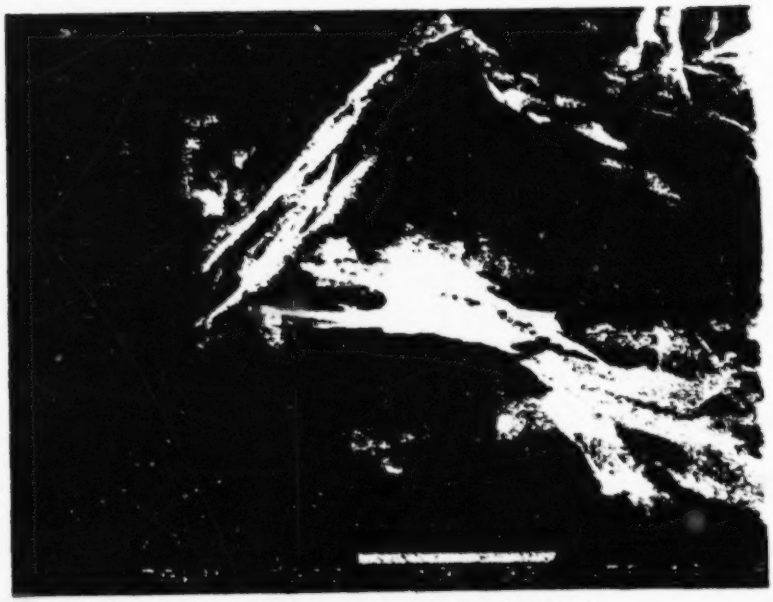


Figure 1. Flow diagram for thiosorbic lime pilot scrubber test.

a. Crystals from Run 2 (5000X).



b. Crystals from Run 4 (3000X).

Figure 2. SEM photographs of solids product.

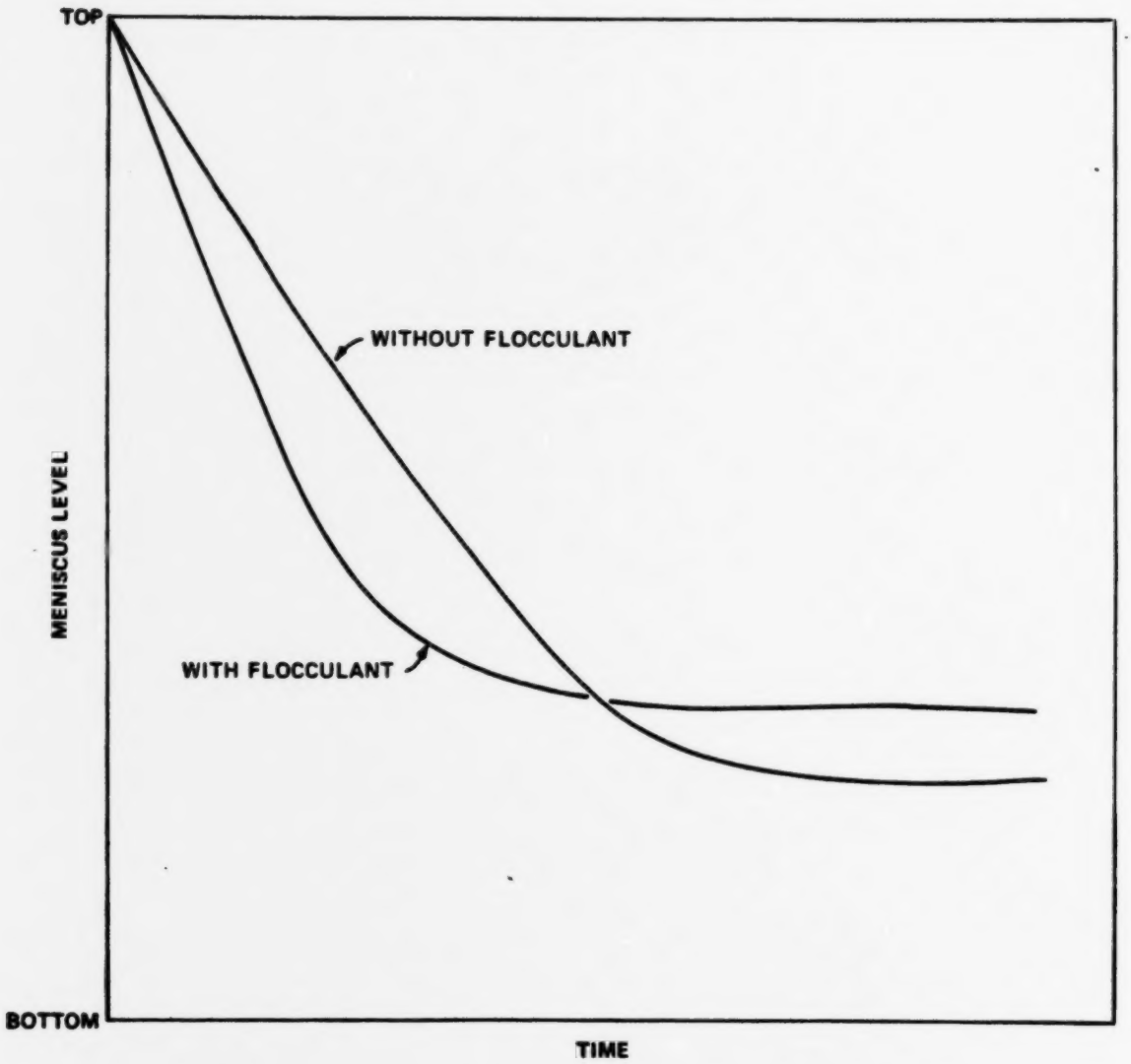


Figure 3. Typical settling curves of hold tank slurry with and without flocculant.

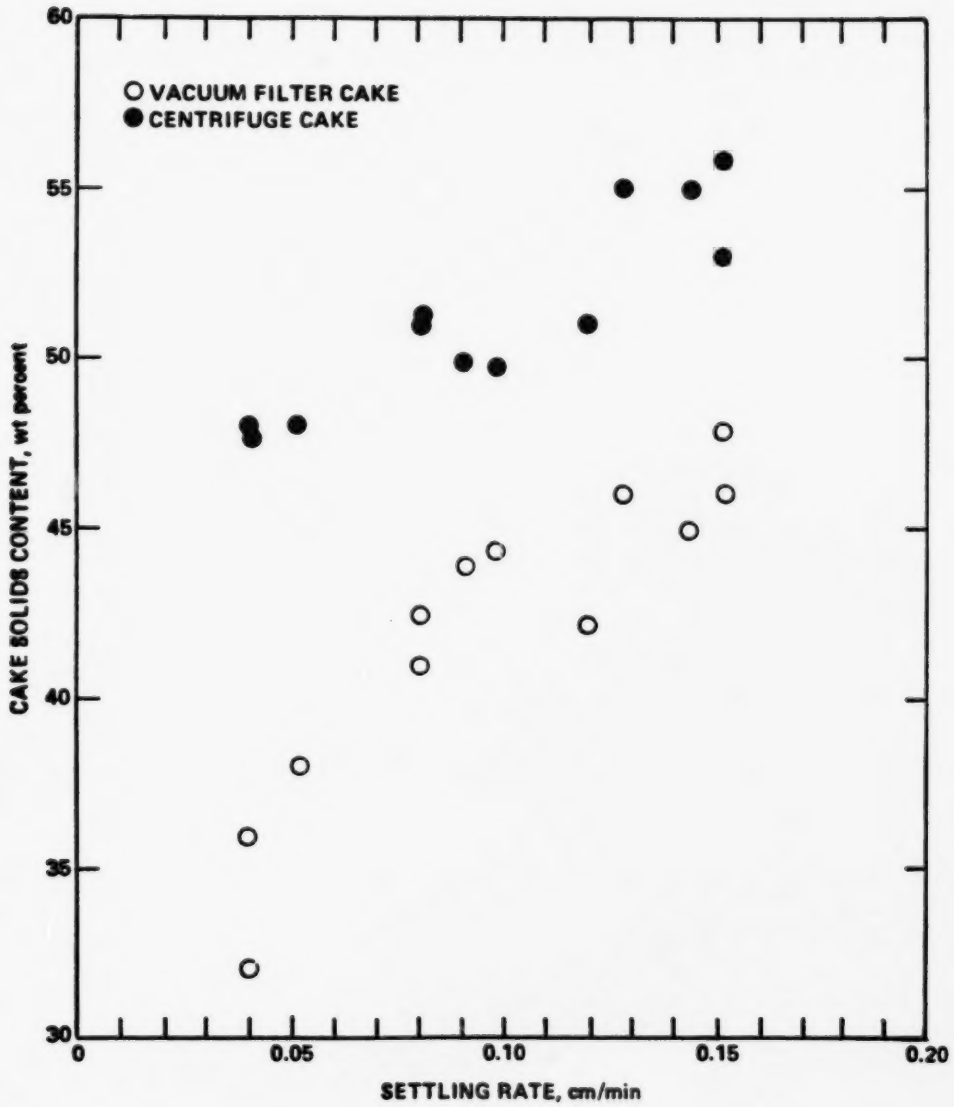


Figure 4. Comparison of cake insoluble solids content from a centrifuge and a rotary drum vacuum filter.